Environmentally friendly phthalocyanine catalysts for water decontamination—Non-photocatalytic systems

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ABSTRACT

Macrocyclic porphyrin-like compounds known as phthalocyanines (Pcs) have been shown to produce singlet oxygen species upon illumination with light of an appropriate wavelength. Singlet oxygen is an effective agent for complete oxidation of common water-soluble pollutants including chlorinated phenols. The most active are, in this respect, phthalocyanines bearing Al, Zn and Si central atoms. Although these compounds were proofed to be virtually non-toxic, the presence of the Al^{3+} and Zn^{2+} ions may contradict this. On the other hand e.g. iron phthalocyanine (FePc) does not represent any danger from this point of view. However, due to the specific coordination of its central metal ion and also because of the number of electrons occupying its valence orbitals, the FePc cannot be effectively activated by the photon flux. Here we report on an alternative system in the dark. It is based on the initial catalytic decomposition of various peroxo substances by metal Pc, producing oxidising species which can decompose chlorinated phenols. A series of Pcs and peroxo substances were compared and the reaction system optimised. It was shown that the highest activity was revealed for the system comprising of FePc and tert-butylhydroperoxide. Iron phthalocyanine was also successfully immobilised on an Al_2O_3 solid matrix, and this heterogeneous system was tested analogously to the homogeneous one. Virtually zero leaching of the anchored complex was detected and the activity was found to be comfortably high.

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1. Introduction

Phthalocyanines (Pcs) were initially described in 1930. Since that time many applications have appeared, those based on their extensive and distinctive colour properties have dominated [1,2]. Their colour depends partly on the substitution of the Pc skeleton, presence or absence of a central atom, its character (the population of its valence band) and on the crystal modification [3]. Phthalocyanines reveal unusual molecular stability caused by the ideal conjugation of double bonds and the symmetrically coordinated central atom in the aromatic skeleton [3], and also, importantly for this communication, virtually zero toxicity [4–6]. Because of their stability and light absorption in characteristic regions of the visible part of spectrum, phthalocyanines have traditionally been used as pigments and dyes [3,7]. Nevertheless, recently, other important applications have appeared based on

their ability to generate an active species upon light absorption. These photoinduced events may occur [8–10] due to the ability of some phthalocyanines to excite ground-state molecular oxygen ($^3O_2$) to highly active singlet oxygen ($^1O_2$). However, it must be noted that, as clearly verified in our recent works [11–13], only phthalocyanines containing transition metal ions with a closed valence shell such as Al^{3+}, Si^{4+} or Zn^{2+} are efficient photocatalysts in the production of $^1O_2$. Those containing metal ions with partially filled d-orbitals such as Co^{2+} and Cu^{2+} tend towards rapid extinction of their excited triplet states [14–16].

Singlet oxygen is an extremely effective agent for complete oxidation of common pollutants of water including chlorinated phenols. Especially in the developing countries, trace chemical pollution is not understood as the major health risk in comparison with water-borne infectious diseases. Chlorination is always the first option to kill bacteria, however, this may lead to the unavoidable substitution of the Cl atom to the aromatic ring skeleton of phenol. And, as it is generally known, phenol, a non-biodegradable substance, is nearly always present in water in the urban areas of such countries. The most active (in the respect of

chlorinated phenols decomposition with singlet oxygen) are phthalocyanines bearing Al, Zn, Si central atoms [11–13]. Despite these compounds were repeatedly proofed and reported as virtually non-toxic [4–6] introduction of species with Al and Zn atoms to the environment is problematic. The presence of Al and Zn may pose a risk in terms of toxicity. Iron phthalocyanine, on the other hand, does not represent any danger from this point of view. However, due to the specific coordination of its central metal ion and also because of the number of electrons occupying its valence orbitals, the FePc molecule cannot be effectively activated by the photon flux. This phthalocyanine may be used in a hydrogen peroxide activated catalytic decomposition of some undesirable water-soluble compounds [17,18].

Here we report on a system based on the initial catalytic decomposition of various peroxo substances (hydrogen peroxide, hydrogen peroxide modified with urea, peroxyacetic acid and tert-butylhydroperoxide) in small amounts by sulfonated metal Pcs in the homogeneous phase, producing oxidising species sufficiently active for complete decomposition of chlorinated phenols. Iron phthalocyanine was also successfully immobilised on the Al_2O_3 solid matrix and this heterogeneous system was tested analogously to the homogeneous one.

This paper is a continuation of our recent works [11–13] reporting on effective photoinduced catalytic oxidation activity of Al, Zn, Si and metal-free Pcs in decontamination of water polluted with chlorinated phenols.

2. Experimental

2.1. Catalysts

Phthalocyanines used in this work (NiPc, CoPc, FePc, TiPc, CuPc, SiPc, ZnPc, AlPc) as catalytic species for decomposition of peroxo substances were lab-made and produced with the highest possible purities. Here, only brief information is provided, details are available elsewhere [1,19–22]. NiPc, CoPc, FePc and CuPc were prepared from corresponding metal chlorides (Aldrich) and phthalodinitrile (Fluka, molar ratio 1:4) in an excess of nitrobenzene (Penta). The mixture was stirred for 6 h at its boiling point with a catalytic amount of ammonium molybdenate (Fluka) and continuously stripped with gaseous NH_3. Then, nitrobenzene was filtered off, the crude Pc washed with methanol (Penta) and finally refined by precipitation from concentrated sulfuric acid (Penta). AlPc was prepared by the method [19] modified with addition of high boiling solvent (octan-1-ol). Another alternative method was performed for the production of SiPc and TiPc, where phthalodinitrile was mixed with metal butoxide (in molar ratio 4:1), in presence of urea and quinoline as described in [20]. SiPc was also prepared on mixing $SiCl_4$ with 1,3-diiminoisoindoleine (molar ratio 1:2) in the presence of quinoline [21]. The next necessary step was sulfonation because the Pc complexes are virtually insoluble in water. This methodology was described carefully in our previous articles [11,12,22].

Immobilisation of the Pc complex was achieved according to the method developed by Augustine et al. [23]. In our team it has been repeatedly employed for supporting Ru-biphosphine catalytic stereoselective complexes for asymmetric reactions [24]. This approach relies on heteropolyacids as spacers between the inorganic surface and the catalytic active phase [25]. Phthalocyanines were deposited onto the surface of alumina (CAMAG, $S_{BET} = 160\ m^2\ g^{-1}$). Typically, 1.5 g of Al_2O_3 was suspended in 30 ml of methanol. Then 386.7 mg (0.15 mmol) of phosphotungstic acid hydrate (Merck, PTA) was dissolved in 25 ml of methanol and this solution was added drop-wise into the stirred alumina suspension. The agitation had continued for one day at room temperature. The liquid was removed from the solid residue and it

was again suspended in 30 ml of methanol. Finally 56.8 mg (0.1 mmol) of the Pc complex was dissolved in 40 ml of dimethylformamide and this solution was dropped slowly to the mixed suspension (one more day). The solution was removed and the solid residue washed with methanol until a colourless solution was obtained. Light greenish blue solid material was dried at 25 °C for 2 h in vacuum and for one day in the laboratory oven. Leaching of the complex was verified by mixing it in water with hydrogen peroxide or tert-butylhydroperoxide (Kodak Eastman) at 25 °C for 1 h with aid of AAS (A-B 372, PerkinElmer) and UV–vis spectrophotometer (Cary 100, Varian). It must be noted that the leached amount was insignificant. Surface images of the FePc immobilised complex were taken with help of SEM microscope Hitachi 520. FTIR spectra of the support, the "free" complex and the heterogenized sample were recorded on a Bio-Rad FTS–65 A spectrophotometer in KBr pellets.

2.2. Typical experiment

Catalytic experiments were carried out isothermally (25 °C, exceptionally at 40 °C) at pH = 7 (TitraLab TIM 856 combined with a pH electrode) in a simple laboratory arrangement comprising a magnetically stirred glass vessel (50 ml), sample probe and thermal insulation. 4-chlorophenol (4CP) (Fluka) was chosen as a model compound. Oxygenating species were released by means of decomposition of peroxo compounds – hydrogen peroxide, hydrogen peroxide modified with urea, peroxyacetic acid and tert-butylhydroperoxide. It must be accentuated that the reaction system was carefully covered with a black tape and a black foil to prevent any contact of the Pc molecules with light. The reaction volume was always 25 ml, concentration of 4-chlorophenol (Merck) 1×10^{-4} mol/l ($n_{4\text{-CP}} = 2.5 \times 10^{-6}$ mol), the amount of phthalocyanine 5 mg/l ($n_{Pc} = 1.75 \times 10^{-7}$ mol). The typical amount of peroxosubstances was 1.5×10^{-4} mol. In the case of experiments with heterogenized catalyst, the concentrations of 4CP and peroxosubstances were the same as in the homogeneous phase. The catalyst amount was 5.37×10^{-6} mol of FePc anchored on 150 mg of Al_2O_3 support. Samples of reaction mixtures were analyzed by HPLC (Shimadzu LC 20A Prominence) with MERCK LiChroCART 125-4 column and with Lichrospher RP-18 stationary phase. Methanol (HPLC grade, Fluka) to water (HPLC grade, Fluka) mobile phase ratio was set up to 40/60. Detection wavelength was chosen at the maximum absorption for 4-chlorophenol (298 nm).

3. Results and discussion

As already discussed a series of metal phthalocyanines (NiPc, CoPc, FePc, TiPc, CuPc, SiPc, ZnPc, AlPc) were employed in the dark in combination with peroxo substances for oxidative decomposition of phenol substituted with Cl in para position. This model compound represents a typical pollutant appearing in small quantities in drinking water due to chlorination and parallel trace contamination with phenol.

Most of the used organometallic complexes coordinate inside of their molecules metal atoms which may represent, upon practical use, some potential environment risk. This is true despite the Pcs are typically very stable, also at elevated temperature [26], and as shown recently [12,13], they do not decompose significantly when exposed to wavelengths exactly matching their absorption bands. However, it is obvious that from the series of the tested phthalocyanines, only FePc might be considered to fulfil the requirements of the environment friendly chemical agent (Note: It is kin with haemoglobin, Fig. 1). On the other hand, FePc was identified as virtually unable to produce singlet oxygen upon illumination with a corresponding photon flux unlike AlPc, ZnPc and SiPc [12]. It belongs to the similar family of metal Pcs such as
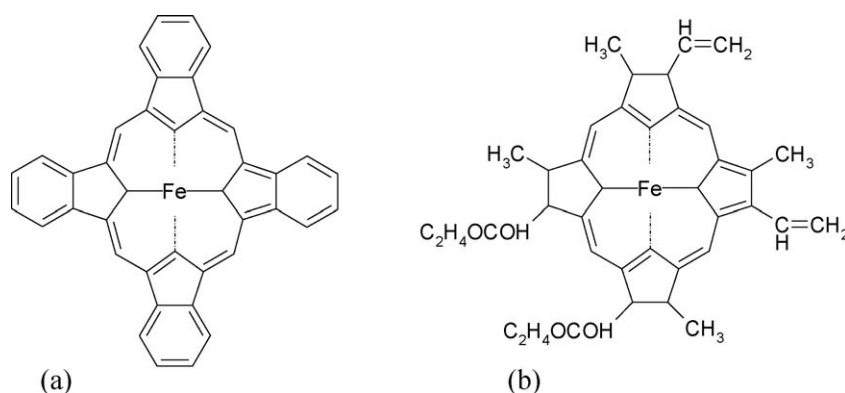
Fig. 1. Molecular structures of (a) Fe phthalocyanine and (b) haemoglobin.

Co and Cu phthalocyanines. Their excited triplet states tend to extinct rapidly and thus the photoactivity is depressed.

The reaction system in the dark based on the catalytic role of the Pc molecule toward decomposition of a simple peroxo compound and forming active oxygenating species is an alternative option. Initially the group of eight metal phthalocyanines was introduced and compared in oxidation of 4-chlorophenol (4CP) with hydrogen peroxide. The complete reaction scheme of this decomposition was repeatedly described in the literature [17,18]. Here we report only data on diminution of 4CP relative concentration in time despite the whole reaction cycle being followed using HPLC and LCQ (mass spectroscopy) analytical tools. Introduction of the very complex system of parallel and consecutive reactions, with a number of intermediates (quinone and hydroquinone are principal intermediates in equilibrium), would complicate the primary purpose of this research. It is seen (Fig. 2) that conversions of 4CP were overall very low (<10%), with some exception of FePc. However, even in this case it reached only 25%. As introduced in the experimental part, the oxidations were carried out at 25 °C and in few cases with FePc also at 40 °C. Increase of the conversion with the temperature rise was, from a practical point of view, insignificant (from 25% to 30%).

The next series of experimental runs were performed with peroxyacetic acid instead of hydrogen peroxide. Fig. 3 shows the comparison of reactions with and without FePc. First it must be accentuated that the effectiveness of this oxidation agent outperformed hydrogen peroxide flagrantly (75% conversion vs. 25% conversion). Second, the substantial role of presence of phthalocyanine was evident. Nevertheless, some oxidation also occurred only with peroxy acid (∼10% conversion).

The last tested oxidation agent was tert-butylhydroperoxide (TBHP with FePc). Its performance is compared with other agents in Fig. 4. Total conversion of 4CP was achieved at the interval when the system with peroxyacetic acid reached the ∼70% level, with hydrogen peroxide the ∼20% level, and with hydrogen peroxide + urea the ∼3% level. Not surprisingly, when other Pcs from the original series of the tested samples were used in experiments with TBHP, their performance was similarly poor as with hydrogen peroxide. It might be interim-concluded at this point that FePc/TBHP/dark represents a suitable system for efficient decontamination of water containing a chlorinated phenolic compound.

Concentration of the most important agent of the designed and optimised decontamination system, FePc, is also quite low (5 mg/l). Furthermore, virtually zero toxicity of FePc and simple removability by adsorption, e.g. on active charcoal, are other assets. In spite of these facts, it might be practically useful to introduce this agent to the reaction in the immobilised form. It would ease its separation and potentially allow a repeated use. There have been many methods described for the effective surface anchorage of complex organometallics [27]. In one of our parallel research directions we follow stereoselective catalytic processes carried out with help of optically pure Ru–BINAP complexes [24].
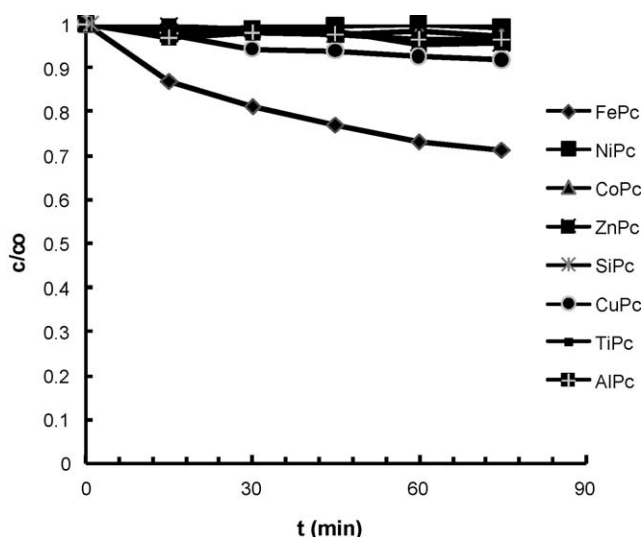

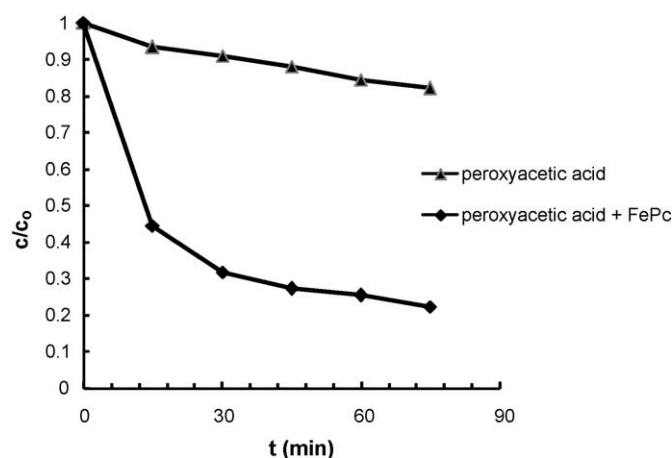**Fig. 2.** Oxidation of 4CP with hydrogen peroxide in presence of the series of Pcs.

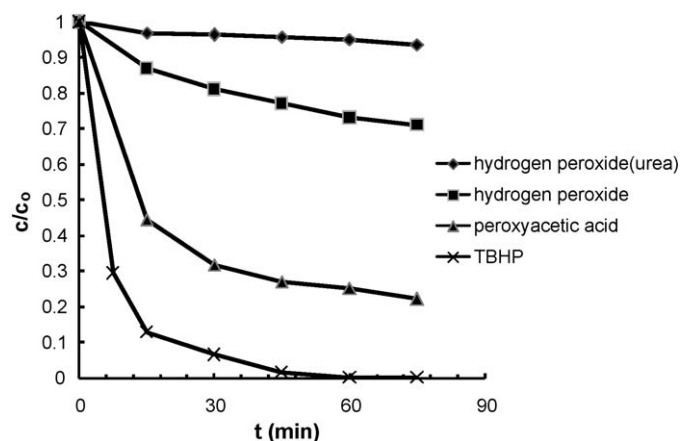**Fig. 3.** Oxidation of 4CP with peroxyacetic acid with and without FePc.

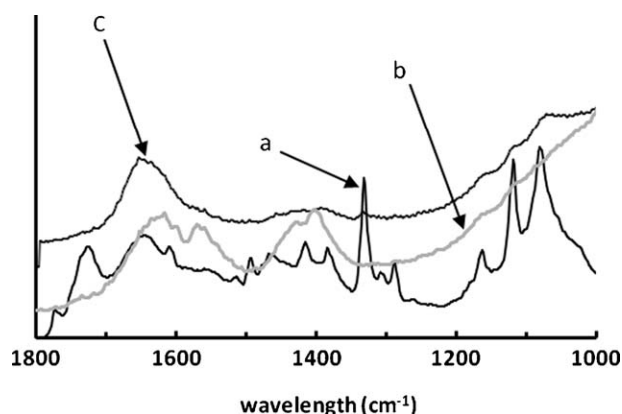**Fig. 4.** Comparison of different peroxo agents in the system with FePc.

Fig. 5. FTIR spectra of (a) FePc, (b) Al_2O_3 and (c) FePc/PTA/Al_2O_3.

These quite expensive species are synthetically difficult to be obtained in adequate purities and thus their repeatable use represents an important value. It has been achieved most recently with help of room temperature ionic liquids [28–30], or traditionally by supporting it on various solid matrixes. In this respect the simple approach using the Keggin's type of hetero-polyacids [31] was found readily accessible. With this knowledge iron phthalocyanine was supported on the surface of alumina following the same strategy [22]. In this first attempt alumina was only one of many options, however, it has been shown to interact with the Keggin's type acids (PTA). Optimisation of this step was not considered as a topic of the current research. The prepared heterogenized catalysts were characterized by IR spectroscopy and FTIR spectra of the support PTA/Al_2O_3, the neat complex FePc and the heterogenized samples were carefully studied. A graphic comparison of these spectra (Fig. 5) clarifies that the homogeneous complex and the heterogenized sample have several similar bands characteristic for phthalocyanines (1332, 1164, 1118 and 1081 cm^{-1}) [32], indicating anchoring of the complex on the solid matrix.

In Fig. 6a a low resolution SEM image of the alumina particles treated with heteropolyacid (PTA) and finally coated with FePc is shown. This shows a uniform particle size of less than 100 nm (data extracted from a higher SEM magnification, Fig. 6b). It is seen that the uniformity is not excellent, which is likely due to the presence of relatively large quantities of phosphotungstic acid hydrate covering the surface of alumina irregularly and accommodating FePc (Fig. 7). There have been many attempts to interpret exactly the role and interactions of heteropolyacid with the anchoring organometallics, and it has not been fully clarified yet [33]. From the practical point of view, however, it is important that leaching is negligible. The catalytic activity of the heterogenized catalyst in the 4CP decomposition is demonstrated in Fig. 8. It is evident that the time necessary for achieving nearly 100% conversion is relatively comparable with experiments carried out in the homogeneous phase. However, as specified in the experimental part, the amount of the catalyst used in heterogeneous phase is significantly higher, which results in different kinetics of the reaction and lower reaction rates regarding the content of phthalocyanine. Despite the lower activity of the heterogenized system, its utilization is still very promising, because it was repeatedly verified that the catalyst does not significantly lose its activity after reuse. The oxidation rate in the second and third reaction run was not suppressed more than 5% of the initial value. This is a powerful catalytic system enabling efficient decomposition of chlorinated compounds from waste waters without any necessity of tedious separation of the catalyst associated with the reactions carried out in the homogeneous phase.
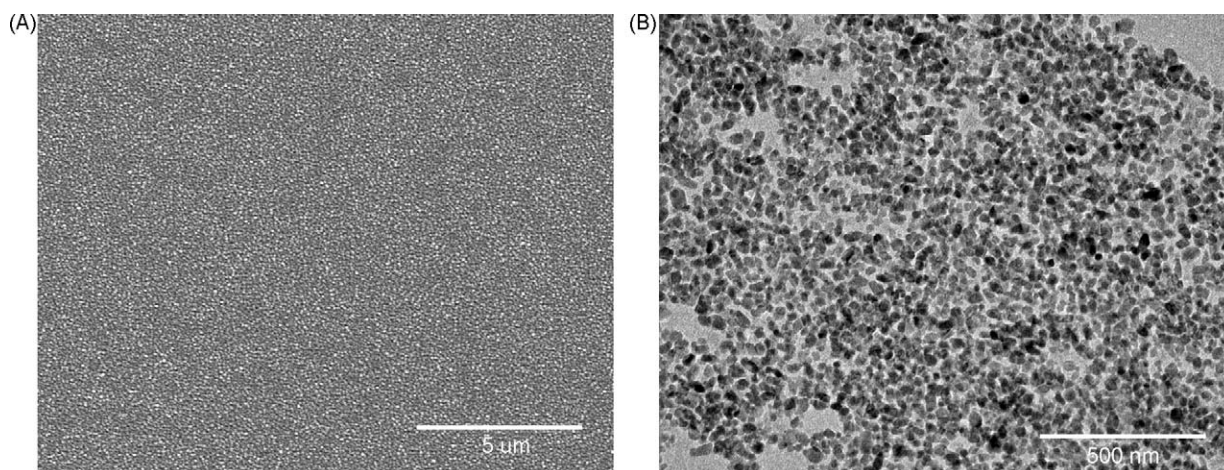

Fig. 6. (a) SEM surface image of FePc/PTA/Al_2O_3. (b) Individual particles of this multistructure catalyst.
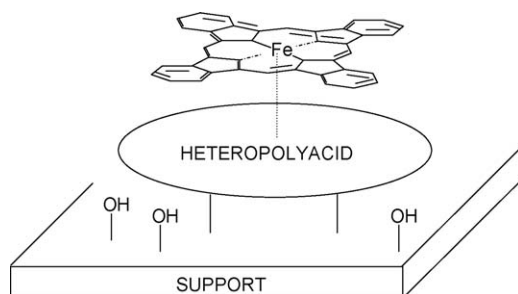
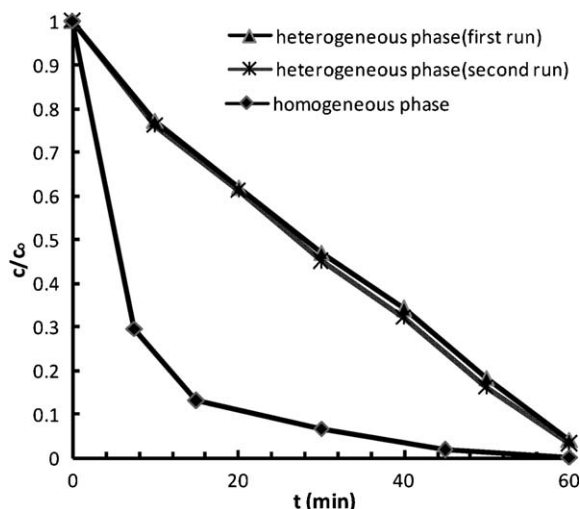**Fig. 7.** Sketch of the role of the Keggin's type acid.

Fig. 8. 4CP oxidation in homogeneous and heterogeneous phase.

4. Conclusion

An alternative system to our recently published studies [11–13] of the water decontamination has been proposed. In the presented work a series of phthalocyanines with different central metal atoms were examined in the respect of their ability to catalyse the decomposition of chlorinated phenols induced by a number of peroxides in the absence of light. All experiments were carried out both in the homogeneous and heterogeneous phase and it was confirmed that the most active system for the 4CP decomposition is represented by the combination of FePc and TBHP, other studied phthalocyanines might be considered as virtually inactive. As expected, the best catalytic performance was observed in the homogeneous phase, but preliminary studies with the catalyst anchored on the alumina solid matrix using Keggin's type heteropolyacid exhibit satisfactorily high reaction rates. Taking into account the recyclability of the catalyst and its stable catalytic performance after reuse, the utilization of Pc/heteropolyacid/solid matrix catalytic system is very promising and will be subjected to our further research.

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